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HIGH DIELECTRIC CONSTANT POLYMER FILM CAPACITORS (PREPRINT)

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14. ABSTRACT Pulse-forming networks (PFNs) are critical for many pulsed power applications and they perform the conversion of prime electric energy into short pulses needed to energize large loads. They require high energy density, fast discharge speed (milliseconds to nanoseconds) capacitors. Medical defibrillators also require high performance capacitors that can deliver pulsed energy to the patient heart in approximately 5 milliseconds at 800 volts (implantable) or over 2,000 volts (external). Current commercial electrostatic capacitors usually have an energy density well below 3 J/cc due to the limitation of dielectric material performance and reliability constraints. The capacitors usually occupy a large fraction of the volume and contribute to the major cost in both the PFNs and the medical devices. The bulky size of capacitor components severely impedes the miniaturization of many electronic devices, although other active components have observed dramatic size reduction in the last twenty years. <div style="text-align: right;"><i>Abstract concludes on reverse →</i></div>						
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14. ABSTRACT (concluded)

The energy density (UE) of a linear dielectric material is proportional to its dielectric constant (K) and the square of its dielectric breakdown strength (DBS). Therefore, high K and DBS are critical to achieve a high energy density in capacitors. DBS is determined by both intrinsic and extrinsic (process-related) factors, but there is a general consensus that except for very thin films deposited on a substrate, the breakdown in practical components is limited by defects introduced during film processing. There have been many improvements over the last 10 to 20 years in polymer resin purity, capacitor film quality, metallization design, and capacitor fabrication so that energy densities of 1 to 3 J/cm³ are now available with predictable lifetime for mission critical applications. It is uncertain if more process improvements can be expected to yield further energy density increase, but there is little doubt the progress will be slow and evolutionary. Therefore, materials with significantly higher dielectric constant are required to achieve breakthrough in high energy density film capacitors.

In this paper, we present our recent progress in the development of high-K polymer dielectric materials, the commercial scale production of high-quality capacitor film, and the test of our first generation prototype capacitors.

High Dielectric Constant Polymer Film Capacitors

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Introduction

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The energy density (U_E) of a linear dielectric material is proportional to its dielectric constant (K) and the square of its dielectric breakdown strength (DBS). Therefore, high K and DBS are critical to achieve a high energy density in capacitors. DBS is determined by both intrinsic and extrinsic (process-related) factors, but there is a general consensus that except for very thin films deposited on a substrate, the breakdown in practical components is limited by defects introduced during film processing. There have been many improvements over the last 10 to 20 years in polymer resin purity, capacitor film quality, metallization design, and capacitor fabrication so that energy densities of 1 to 3 J/cm³ are now available with predictable lifetime for mission critical applications. It is uncertain if more process improvements can be expected to yield further energy density increase, but there is little doubt the progress will be slow and evolutionary. Therefore, materials with significantly higher dielectric constant are required to achieve breakthrough in high energy density film capacitors.

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High-K Polymeric Dielectrics

Commercial polypropylene (PP) capacitor film has a low K of 2.2 and has been the most commonly used dielectric in film capacitor industry for more than 50 years.[1,2]

There are several high- K polymeric dielectric materials that have been developed at Penn State University during the past 10 year.[3-8] The first is a high-energy electron irradiated Poly(vinylidene fluoride-co-trifluoroethylene) copolymer (PVDF-TrFE). PVDF-TrFE is a classic ferroelectric polymer with Curie transition temperature (T_C) above 60 °C, depending on the composition. The irradiated PVDF-TrFE is converted to a relaxor ferroelectric material with the disappearance of the Curie transition and the giant dielectric constant above 50 at room temperature.

Similar high-K was also achieved by a chemical modification. A third monomer such as chlorotrifluoroethylene (CTFE) or 1-chloro-1-fluoro-ethylene (CFE) was introduced into PVDF-TrFE to obtain a terpolymer. The CFE or CTFE is bulkier than VDF and TrFE and they convert the all trans beta crystalline phase of PVDF-TrFE to trans-gauge alpha crystalline phase. Similar to the irradiated copolymer, the terpolymers are also relaxor ferroelectric materials with $K > 50$ at room temperature. The terpolymers are thermoplastic and can be processed into thin capacitor film by either solvent cast or melt extrusion/orientation.

The dielectric constant of the high-K polar fluoropolymers was further improved by the development of nanocomposites. With well-controlled morphology, dielectric constant over 1,000 has been achieved in PVDF-TrFE-CFE/CuPc nanocomposites.

Other PVDF-based copolymers have also been evaluated by us for high-energy density film capacitor applications since 2005. It has been found that the copolymers have significantly better performance than the PVDF homopolymer. Figure 1 presents the dielectric constant of these high-K polymers at 1 kHz as a function of temperature.

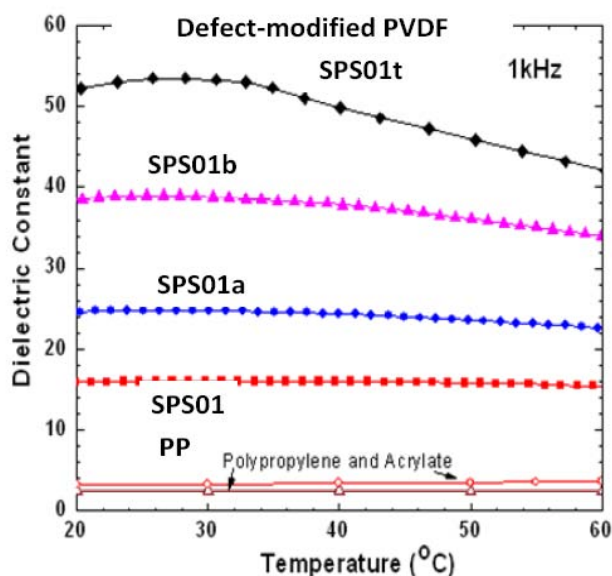


Figure 1. Dielectric constant of SPS polymers at 1 kHz. They are purely thermoplastic polymers without any filler and high quality capacitor film can be produced by either melt extrusion or by solvent casting.

While the dielectric constant of these modified PVDF is high, they also have high dielectric breakdown strength for high energy density applications.

With the high dielectric breakdown strength and high dielectric constant, the SPS capacitor film has significantly higher energy density than commercial PP capacitor film. Figure 2 compares the discharged energy density of SPS film and PP film based on the test of $\sim 1 \text{ cm}^2$ sample size. The energy density was directly measured using a Sawyer-Tower circuit at 10 Hz at voltages up to 10 kV.

It can be seen that energy density of 27 J/cm^3 can be obtained in SPS03. At $500 \text{ V/}\mu\text{m}$, SPS01, SPS03, and PP have energy density of 17.6, 12.8, and 2.7 J/cm^3 , respectively. SPS01 and SPS03 have slightly different chemical compositions.

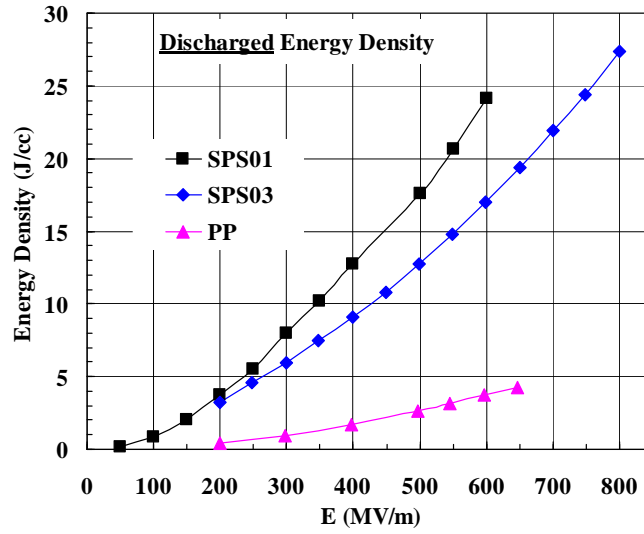


Figure 2. Discharged energy density of SPS high-K film and commercial PP film as a function of applied electric field. The data are directly measured values and not theoretical prediction.

Capacitor Film Production

While high dielectric breakdown strength and energy density have been achieved in lab-scale capacitor film samples, it is critical to scale up the capacitor film production to produce large rolls of high quality capacitor film for practical applications. Large size pulsed power film capacitors can use capacitor film with area well above 1 m², and the capacitor film should be free of pinhole and have uniform thickness in such large area. Other requirements include thermal shrinkage, surface roughness, mechanical strength, and surface tension, etc.

We have performed pilot-scale capacitor film production using melt-extrusion biaxial orientation process with a special resin that Solvay Solexis and Strategic Polymer Sciences, Inc. jointly developed and produced for capacitor application. The pilot film line can produce capacitor film up to 2 m wide and run at speed over 200 m/min. Capacitor film rolls with thickness from 2 μm to 10 μm have been successfully produced. The length of the pilot film roll is over 3,000 m and the thickness uniformity is better than ±5%.

Figure 3 shows a picture of SPS capacitor film rolls.



Figure 3. Ultra-thin SPS capacitor film produced by melt-extrusion and biaxial orientation.

It should be noted that the melt extrusion process is widely used by capacitor film industry to produce PP and PET capacitor film. Commercial capacitor film line can produce film with thickness below 1 μm thick. The large scale solvent-free production can significantly reduce the capacitor film cost as compared with the solvent-based capacitor film production, in addition to the environmental advantage.

Figure 4 compares the dielectric breakdown strength of SPS high-K capacitor films and the commercial 4.8 μm thick PP capacitor film. The SPS capacitor films have thickness of 5 μm . The dielectric breakdown test was performed using metallized PP capacitor film as electrodes with tested area of 2 cm by 2 cm.

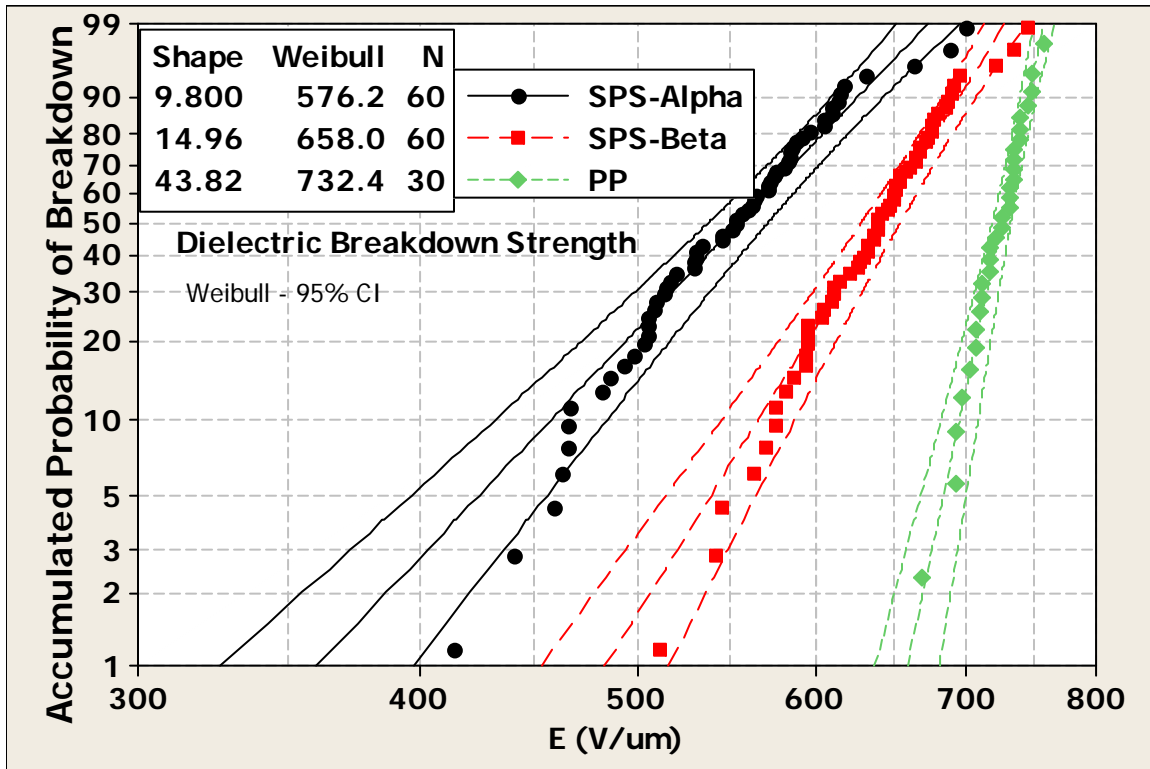


Figure 4. DC dielectric breakdown strength of SPS high-K capacitor film and commercial 4.8 μm PP capacitor film. 60 specimens were tested for each SPS capacitor film to obtain statistic significance.

Following the same test protocol, the commercial PP capacitor film has dielectric breakdown strength (DBS) of 732 $\text{V}/\mu\text{m}$. The SPS-Alpha capacitor film has DBS of 576 $\text{V}/\mu\text{m}$ and it was improved to 658 $\text{V}/\mu\text{m}$ in the Beta film. SPS is currently developing a new generation of capacitor film with improved quality to compete with commercial PP capacitor film. It should be pointed out that SPS high-K capacitor film already offered a much higher energy density than PP even with current generation film.

Prototype Capacitors

The high-K film was metallized and wound into prototype capacitors with different capacitances. The metallization is a thin layer of aluminum with high surface resistance for high dielectric breakdown strength.

10 μF capacitors made with 5 μm thick film exhibit high dielectric breakdown strength and high energy density. Most of the 10 μF capacitors can pass 1,500 V breakdown test, and more than half of them can survive 2,000 V

charge-discharge test. The capacitor was charged under constant current to the preset voltage, and then discharged to a load resistor. The discharged energy density was calculated from the discharging process by numerical integration.

Figure 5 shows pictures of the prototype capacitors. The 120 μF capacitors were made with 2.5 μm thick SPS high-K film. It has capacitance density of 7.01 $\mu\text{F}/\text{cm}^3$ or 4.11 $\mu\text{F}/\text{g}$. For comparison, commercial PP capacitors with 3 μm thick film have capacitance density of 0.62 $\mu\text{F}/\text{cc}$ or 0.45 $\mu\text{F}/\text{g}$. This clearly demonstrates the potential miniaturization of many electric devices by using SPS high-K film capacitors.

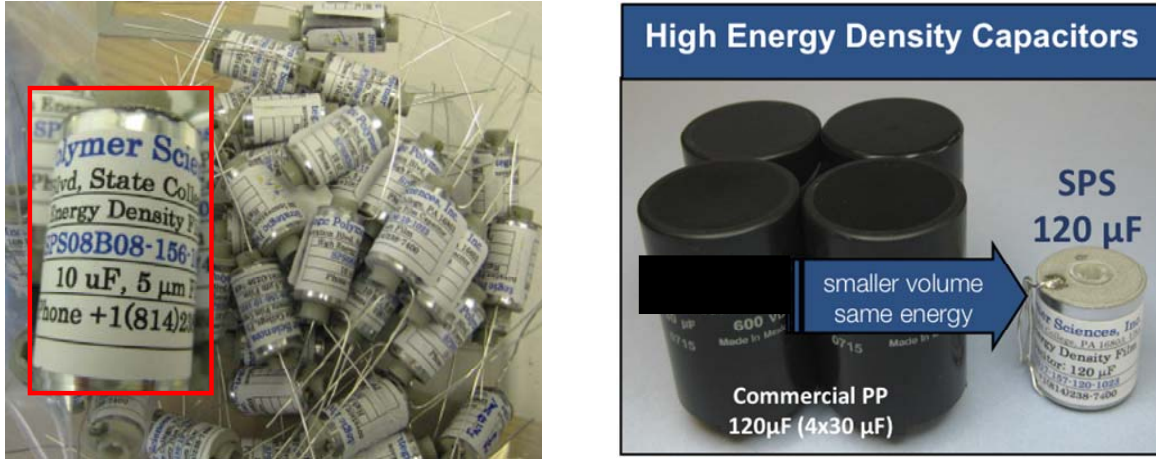


Figure 5. Prototype SPS high-K film capacitors.

Table 1 compares the performance of SPS high-K film capacitors with commercial PP capacitors made with 3 μm PP film. It should be noted that SPS prototype capacitors are unpackaged, however, it will be still have much higher capacitance density even packaging, which may add 10~20% volume.

Table 1. Comparison of SPS High-K Film Capacitors and Commercial PP Capacitors

	Capacitance (μF)	Film Thickness	Diameter (mm)	Height (mm)	Volume (cc)	Volume ($\mu\text{F}/\text{cc}$)	Weight (g)	Weight ($\mu\text{F}/\text{g}$)
Commerical	30	3 μm	35	50	48.1	0.62	66.6	0.45
SPS-1	43	3.1 μm	19	32	9.1	4.74	15.9	2.70
SPS-2	85	3.1 μm	24.6	32	15.2	5.59	27.8	3.06
SPS-3	120	2.5 μm	26.1	32	17.1	7.01	29.2	4.11

Figure 6 presents the discharged energy density as a function of applied electric field.

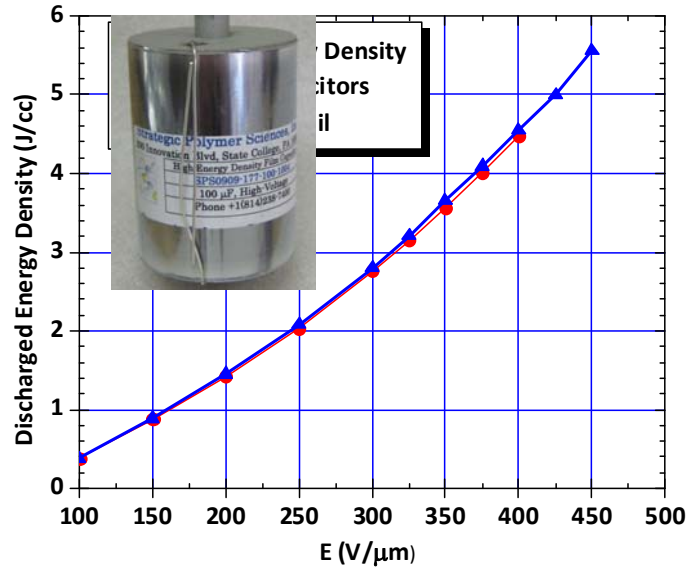


Figure 6. Discharged energy density of SPS high-K prototype capacitors with 100 μF capacitance.

In the preliminary test of the 100 μF prototype capacitors, energy density above 5 J/cm^3 has been obtained, although no systematic lifetime has been tested. Even de-rated to 400 $\text{V}/\mu\text{m}$ for high reliability, the capacitor has energy density above 4.5 J/cm^3 .

On the other hand, the capacitor can deliver energy at milliseconds time scale. Figure 7 presents the discharging behavior of the prototype capacitors.

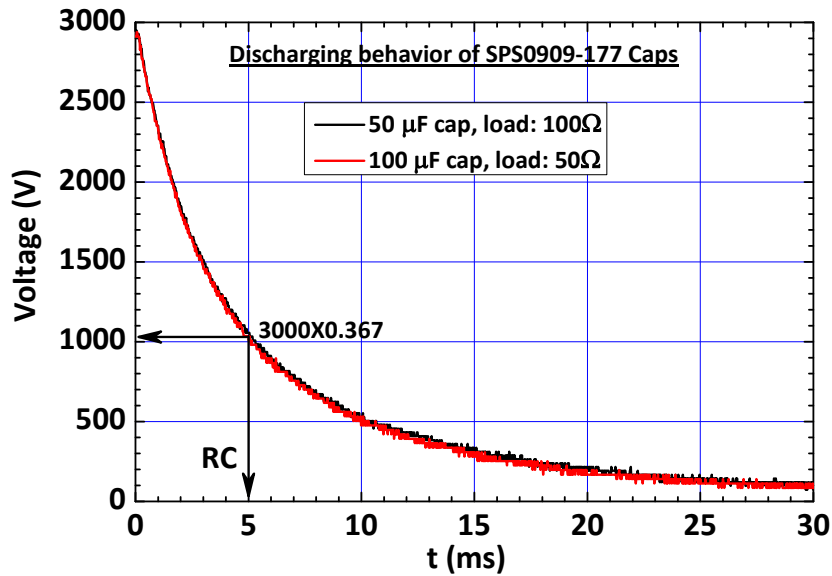


Figure 6. Discharging behavior of SPS prototype capacitors.

The discharge resistors were selected to make the discharge RC constant of 5 milliseconds. It is found that the recorded discharge process approximately follows the theoretical prediction.

The leakage current of the capacitors decreases with longer DC holding time. For example, at 23 °C and 375 V/ μ m, the 100 μ F capacitor has leakage current of 500 μ A and 270 μ A after applying DC voltage for 1 minute and 3 minutes, respectively. This equals to an insulation resistance of approximately 1,000 μ F·M Ω at 375 V/ μ m.

Summary

We have developed several polymer dielectrics with tunable high dielectric constant from 10 to 50 and dielectric breakdown strength over 600 MV/m with graceful failure characteristic. Discharged energy density over 25 J/cc can be achieved based on results from direct charge-discharge measurement in lab-scale capacitor film sample.

While the high energy density of SPS polymer high-K materials has been demonstrated in lab-scale small area capacitor film samples and the pilot production of ultra-thin capacitor film has been performed with inexpensive melt extrusion biaxial orientation process, it is clear that the capacitor film quality still needs significant improvement to achieve the high energy density as measured in the lab-scale film sample. Specifically, 1 cm² size lab-scale capacitor film has dielectric breakdown strength above 750 V/ μ m (comparable to PP film) and energy density above 27 J/cc, the 50 μ F prototype capacitors have breakdown voltage only about 500 V/ μ m. It is believed that the contamination in the resin and the film significantly reduces the dielectric breakdown strength and the energy density in the large prototype capacitors. Therefore, it is critical to produce capacitor resin and film with quality comparable to commercial PP capacitor film to fully transfer the high energy density from lab-scale small area film sample to large size capacitor devices.

Once the film quality of the high-K polymers has been improved and the prototype capacitors can be operated at 600 V/ μ m, energy density of 10 J/cc can be achieved by combining more efficiency capacitor design.

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